

Glass-Like Heat Conduction in High-Mobility Crystalline Semiconductors

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The thermal conductivity of polycrystalline semiconductors with type-I clathrate hydrate crystal structure is reported. Ge clathrates (doped with Sr and/or Eu) exhibit lattice thermal conductivities typical of amorphous materials. Remarkably, this behavior occurs in spite of the well-defined crystalline structure and relatively high electron mobility ($\sim 100 \text{ cm}^2/\text{Vs}$). The dynamics of dopant ions and their interaction with the polyhedral cages of the structure are a likely source of the strong phonon scattering.

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The low-temperature thermal conductivity (κ) of glasses has universal features that have been the subject of experimental and theoretical investigation for many years [1]; at the lowest temperatures ($T < 1 \text{ K}$), $\kappa \propto T^2$, and for $4 \text{ K} < T < 20 \text{ K}$, κ is nearly temperature independent (the "plateau"). The T^2 behavior is attributed to phonon scattering by a broad distribution of two-level systems, whereas the plateau arises from a strong decrease in the phonon mean free path with increasing frequency, e.g. due to Rayleigh scattering from variations in density or bond length. Though typical of amorphous materials, similar thermal conductivity behavior, with κ approaching theoretical minimum values [2], has been observed in some disordered crystalline dielectric materials [3,4]. A common characteristic of these latter systems is the presence of atoms or molecular groups having two or more semi-stable positions, and the absence of long-range correlation between their positions or orientations. Resonant scattering of phonons by these "rattling" entities can also produce a plateau in κ [5].

The search for high-mobility semiconductors with glass-like thermal properties – "phonon glass, electron single crystals" (PGEC's) – was initiated by Slack [6], and motivated by thermoelectric applications [7] which could be substantially improved by the higher figure of merit such hypothetical materials would possess. It was postulated that the group IV elements forming clathrate-structured compounds were potential PGEC's [4]. In this Letter we report the realization of PGEC behavior in crystalline Ge clathrates. Trends in the behavior of the low-temperature lattice thermal conductivity for Si, Ge and Sn clathrates indicate that the glass-like heat conductivity arises from resonant scattering of phonons by vibrations of the dopant ions in their polyhedral cages. The relatively high charge-carrier mobility of these clathrates indicates that the dopant-cage interactions do not substantially degrade the electronic properties.

The sample preparation has been described previously [8]. The specimens are polycrystalline Si and Ge clathrates having the type-I hydrate crystal structure [15], doped with divalent barium (Ba^{2+}), strontium (Sr^{2+}), and europium (Eu^{2+}) ions, and Sn clathrates of the same structure, doped with monovalent Cs^+ . The cubic crystal lattice is a tetrahedral network of Si, Ge or Sn which forms periodic voids or "cages" of 20- and 24-coordinated polyhedra in a 1:3 ratio, respectively. The dopant ions enter the lattice interstitially, residing inside these large cages. X-ray diffraction (XRD) spectra from powdered clathrate samples revealed sharp lines with no phases other than that of type-I clathrate-hydrate ($Pm\bar{3}n$). Trace amounts of Si were detected in the Si-clathrate sample. Electron beam microprobe analysis of a polished surface of each sample confirmed the x-ray results and yielded stoichiometric percentages for each sample. In the case of the Ge-clathrates, scanning tunneling microscopy showed a defect-free structure within the grains. Table I lists some of the physical and electronic properties of these phase-pure, dense polycrystalline samples. Gallium, which substitutes for Si or Ge, was added to compensate for the charge of the divalent dopants. Charge neutrality in the $\text{Cs}_8\text{Sn}_{44}$ compound implies two Sn vacancies per unit cell. A preliminary report [8] on specimens with nominal composition $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ indicates that the carrier concentration and mobility vary with composition. Their relatively high mobilities (up to $100 \text{ cm}^2/\text{Vs}$) in comparison to other thermoelectrics [10] suggest the possibility that the Ga may be ordered in these materials, an issue currently under investigation.

The samples were cut with a wire saw into parallelepipeds with approximate dimensions $5 \times 2 \times 2 \text{ mm}^3$. Steady-state thermal conductivity measurements at $T \geq 4 \text{ K}$ were conducted in a radiation-shielded cryostat using a single heater and $25 \mu\text{m}$ -diameter differential chromel-constantan thermocouple. The electrical resistivity and thermoelectric power were measured simul-

taneously; room-temperature values are listed in Table I. Heat losses due to radiation and conduction through the leads were measured in separate experiments and the data corrected. These losses were 10-15% near room temperature and < 5% for $T < 120$ K. The absolute accuracy in κ is $\pm 10\%$, limited by uncertainty in the thermocouple junction separation. Measurements at $T < 4$ K were conducted in a dilution refrigerator using a similar technique with two thermometers.

Figure 1 shows lattice thermal conductivities, $\kappa_g = \kappa - \kappa_e$, in the range $5 \text{ K} < T < 300 \text{ K}$ for the five clathrates listed in Table I. The electronic thermal conductivity, κ_e , was estimated using the electrical resistivities and Wiedemann-Franz law with ideal Lorenz number, $L_0 = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$. Also shown is κ for amorphous germanium (a-Ge) and a-SiO₂ [11]. The $T=295 \text{ K}$ values of κ_g for all of the specimens are small, lying between that of a-SiO₂ and a-Ge, and approaching κ_{min} for Ge, the minimum theoretical value calculated using the model of Slack [2], and taking the minimum mean free path (mfp) of the acoustic phonons as one-half their wavelength [3]. The Sn clathrate exhibits a temperature dependence typical of crystalline insulators, with κ_g increasing with decreasing T approximately as $1/T$, the signature of propagating phonons scattered by anharmonic interactions. For the Si-clathrate, κ_g also increases with decreasing T , but not as strongly, indicating additional scattering at low temperatures. The Ge clathrates have κ_g suppressed below that of the Sn clathrate by more than an order of magnitude at low T . Most striking are the plateaus or minima in $\kappa_g(T)$ for the Ge clathrates, similar to that of a-SiO₂ and other amorphous materials in the range $4 \text{ K} < T < 30 \text{ K}$. This similarity extends to $T < 1 \text{ K}$ as shown in Fig. 2 for the Sr₈Ga₁₆Ge₃₀ specimen; $\kappa_g \propto T^2$ is observed down to $T=60 \text{ mK}$. Our previous estimates of grain-boundary scattering for the Ge clathrates [8] and preliminary κ measurements on Ge clathrates with similar composition and mm-sized grains [10], indicate that grain boundaries are not the source of the glass-like κ in these materials.

To interpret the κ_g data in the absence of experimental studies of the vibrational spectra for these semiconducting clathrates, it is instructive to consider prior work on the thermal conductivity [12] and vibrational properties [13] of type I clathrate hydrates (ice clathrates).

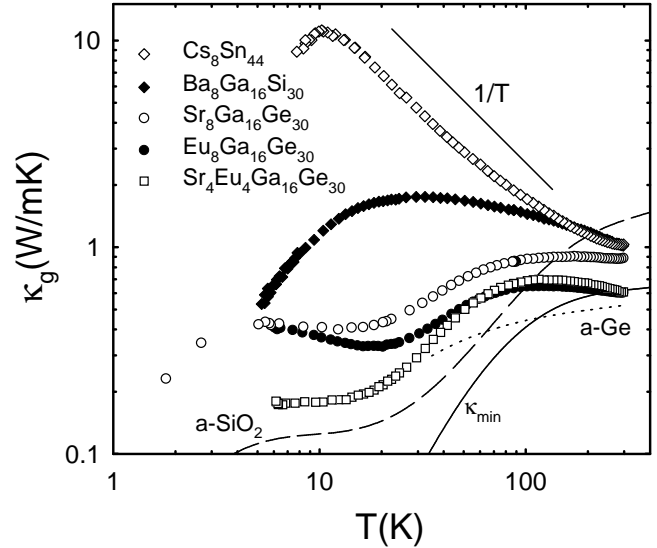


FIG. 1. Lattice thermal conductivity vs. temperature for the five clathrate specimens listed in Table I. The dashed and dotted curves are for a-SiO₂ and a-Ge (Ref. [11]), and the solid curve is the calculated minimum thermal conductivity of Ge (see text).

comprised of water molecules, which encapsulate gas atoms or molecules (guests). Their thermal conductivities are anomalously low and glass like. The qualitative features of the guest-host interactions for these materials are expected to be similar to those of semiconducting clathrates. Neutron scattering studies and molecular/lattice dynamical calculations [14] have established that localized guest vibrations interact strongly with the host acoustic phonon branches in the clathrate hydrates. This interaction arises as an avoided crossing of dispersing phonon branches and non-dispersing guest vibrations of the same symmetry, and yields a resonant damping of heat-carrying phonons at certain points in the Brillouin zone. The guest translational vibration frequencies increase as the size difference between guest and host cage decreases, a natural consequence of stronger restoring forces for the guests. Generally, one expects two prominent resonances, with the lower (higher) frequency corresponding to guest vibrations in the larger (smaller) host cages.

TABLE I. The five compounds of this study with atomic percentages from electron-beam microprobe analysis, lattice parameters, a_0 , average grain sizes, room-temperature electrical resistivities, ρ , and absolute Seebeck coefficients, S .

compound	Elemental atomic %	$a_0(\text{\AA})$	grain size (μm)	$\rho(\text{m}\Omega\text{cm})$	$S(\mu\text{V/K})$
Cs ₈ Sn ₄₄	15.6Cs/84.4Sn	12.113	13.0	59.4	-304
Ba ₈ Ga ₁₆ Si ₃₀	15.5Ba/27.5Ga/57.0Si	10.554	9.6	2.04	-66
Sr ₈ Ga ₁₆ Ge ₃₀	14.8Sr/30.2Ga/55.3Ge	10.731	9.6	12.8	-313
Eu ₈ Ga ₁₆ Ge ₃₀	14.2Eu/28.3Ga/57.6Ge	10.711	5.4	2.52	-152
Sr ₄ Eu ₄ Ga ₁₆ Ge ₃₀	8.2Sr/6.9Eu/28.6Ga/56.4Ge	10.726	12.2	1.00	-88

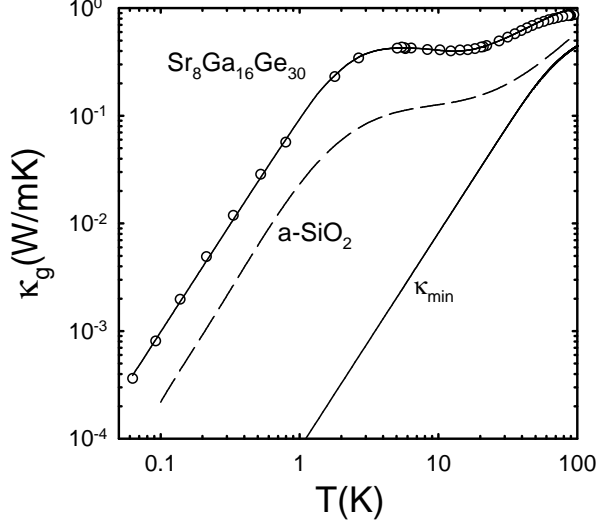


FIG. 2. Lattice thermal conductivity measured from 60 mK to 100 K for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ with a fit (solid curve) to the model discussed in the text (see also Fig. 3). The dashed line is for a-SiO_2 , and the solid curve labelled κ_{\min} is the calculated minimum thermal conductivity of Ge.

Consider the relevant guest and host dimensions for our specimens. The radii of the Ba^{2+} , Eu^{2+} and Sr^{2+} ions are 2.07, 1.91 and 1.90 Å, respectively, from x-ray crystallographic data of the respective telluride compounds with the NaCl-type structure [15]. These dimensions may not be accurate for the Si or Ge-clathrates where the ions reside in large polyhedral “cages”, but the trend in radii should be similar. The Si_{20} and Si_{24} cage radii are estimated to be 2.05 and 2.23 Å, respectively, from XRD data on Si-clathrates doped with alkali metals [16]. XRD also indicates no significant influence of Ga substitution on the average size of the cages. The Ge_{20} and Ge_{24} cages have radii of 2.15 and 2.32 Å, respectively [16]. Thus we expect that Eu^{2+} and Sr^{2+} in the Ge compounds are “looser” in their cages than are Ba^{2+} ions in the Si compound. We infer that the ionic radius for Cs^+ in the Sn clathrate is approximately the same as the cage size from the following analysis. Using data for isostructural K- and Rb-doped Sn clathrates from the literature [17] we plot lattice constant *vs* alkali-metal ion radius [18], and observe that the measured lattice constant for $\text{Cs}_8\text{Sn}_{44}$ is larger than that implied by linear extrapolation on this plot. This suggests that Cs^+ in the cages of $\text{Cs}_8\text{Sn}_{44}$ causes a lattice expansion.

From these observations it is apparent that the magnitude of the $T = 10$ K lattice thermal resistivity, $1/\kappa_g$, correlates with the relative guest/host-cage size mismatch. This motivates our proposal that the plateaus or dips in κ_g for the Ge clathrates are associated with resonant scattering via dopant vibrations. The absence of this behavior in the Sn clathrate and weaker effect in the Si clathrate suggest that the vibrational

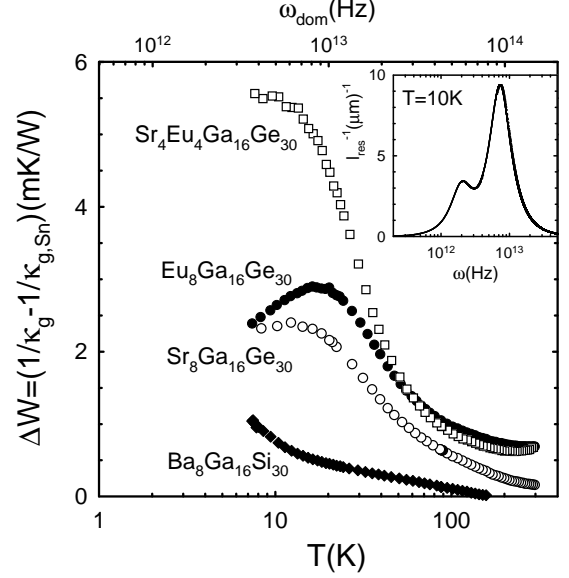


FIG. 3. Difference in the lattice thermal resistivity of each Ge clathrate from that of the Sn clathrate. The frequency scale (upper ordinate) is for dominant thermal phonons ($\hbar\omega = 3.8k_B T$). The inset shows the inverse scattering length at $T = 10$ K for the resonant terms (see text) used to fit the data for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (solid curve in Fig. 2). The parameters were: $C_1 = 3.8 \times 10^6 \text{ m}^{-1} \text{ s}^{-3} \text{ K}^{-2}$, $C_2 = 1.7 \times 10^8 \text{ m}^{-1} \text{ s}^{-3} \text{ K}^{-2}$, $\omega_1 = 1.7 \text{ THz}$, $\omega_2 = 6.3 \text{ THz}$, and $\gamma_1 = \gamma_2 = 0.8$.

frequencies of Cs^+ and Ba^{2+} , respectively, are sufficiently high in energy that a strong interaction with the acoustic phonon branches of the host does not occur for these compounds. To further explore the resonance scattering within this scenario we use the Sn-clathrate data as a reference, computing the difference in thermal resistivity for each of the other clathrates from that of the Sn clathrate, $\Delta W = 1/\kappa_g - 1/\kappa_{g,\text{Sn}}$. These results are plotted in Fig. 3 and, if this interpretation is correct, represent a measure of the thermal resistivity due to resonance scattering in the Si and Ge clathrates. We see that ΔW for the Ge clathrates is peaked in the temperature range 10-20 K. Within the dominant phonon approximation ($\hbar\omega_{\text{dom}} \simeq 3.8k_B T$ for constant mfp) this corresponds to phonon frequencies $\omega_{\text{dom}} \sim 5\text{--}10 \text{ THz}$ (upper ordinate in Fig. 3). The asymmetry of the maxima for the Sr- and Eu-doped specimens suggests the presence of a second, smaller resonance peak at lower frequency.

The $\kappa_g \propto T^2$ behavior at low temperatures implies a phonon mfp inversely proportional to frequency, $l(\omega) \propto \omega^{-1}$. This follows from the kinetic theory expression, $\kappa_g = Cv l/3$ (C and v are the lattice specific heat and sound velocity, respectively), a Debye specific heat, $C \propto T^3$, and $\omega \propto T$ for thermal phonons. The localized tunnel systems (TS) that give rise to this phonon scattering in amorphous materials [1] also yield anomalous features in the specific heat and elastic properties in the

same temperature range. It is plausible that TS's are the source of the scattering in the clathrates. For example, they could correspond to different positions of the dopant ions in their cages; a broadened density of these states might be induced by the random distribution of the dopants. Measurements of specific heat and elastic properties are needed to address this issue.

At $T \leq 40$ K, where $\kappa_g \gg \kappa_{min}$ and phonon transport is an appropriate description, the behavior of κ_g for the Ge specimens can be simulated by integrating the kinetic theory expression, $\kappa_g = (v/3) \int C(\omega)l(\omega)$, with a Debye specific heat and a mfp that is a sum of terms representing TS, resonant, and Rayleigh (R) scattering, $l(\omega) = (l_{TS}^{-1} + l_{res}^{-1} + l_R^{-1})^{-1} + l_{min}$, with [19,20,21],

$$\begin{aligned} l_{TS}^{-1} &= A(\hbar\omega/k_B)\tanh(\hbar\omega/2k_BT) \\ &\quad + (A/2)(k_B/\hbar\omega + B^{-1}T^{-3})^{-1}, \\ l_{res}^{-1} &= \sum_i C_i\omega^2T^2/[(\omega_i^2 - \omega^2)^2 + \gamma_i\omega_i^2\omega^2], \\ l_R^{-1} &= D\hbar^4\omega^4/k_B^4. \end{aligned}$$

The constants A and B are related to microscopic variables describing the TS model [21]. The phenomenological resonance terms are of the form employed previously to describe phonon scattering in ionic crystals [22]. The lower limit on l is assumed to be a constant, l_{min} . Using $v = 3370$ m/s and $\Theta_D = 360$ K appropriate for diamond-structured Ge [23], the solid curve in Fig. 2 was generated for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ using $A = 1.38 \times 10^4 \text{ m}^{-1}\text{K}^{-1}$, $B = 1.5 \times 10^{-3} \text{ K}^{-2}$, $l_{min} = 3 \text{ \AA}$, $D = 1 \text{ m}^{-1}\text{K}^{-4}$ and a sum of two resonance terms shown in the inset of Fig. 3. The TS parameters are comparable to those found for many amorphous solids [21]. The l_{res}^{-1} employed is not unique and the values of ω_1 and ω_2 are sensitive to the value of D in the range characteristic of crystalline materials, $0 \leq D \leq 5 \text{ m}^{-1}\text{K}^{-4}$ (two orders of magnitude smaller than in glasses [21]). Within this range of D , we achieved good fits for resonance frequencies, $0.6 \text{ THz} \leq \omega_1 \leq 2 \text{ THz}$ and $3 \text{ THz} \leq \omega_2 \leq 20 \text{ THz}$. The data for the other Ge specimens could be fitted using the same TS parameters by simply adjusting the magnitudes of the two resonance terms without substantially altering the resonance frequencies. Thus a sum of two resonances has the minimum complexity required to reproduce the range of κ_g behavior we have observed. We expect a “freeze-out” of the guest-ion rattling at low temperatures; this should give rise to static disorder in bond lengths associated with a distribution of the guest-ion positions within their cages. Small energies (≤ 1 K) presumably characterize the separation between these states, and are the origin of the TS.

These unique materials possess interesting and potentially useful properties that call for further investigation. As one of only a few crystalline materials having glass-like thermal conduction, other thermal and elastic properties

at $T < 1$ K are of particular interest.

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